

United States Patent

[11] 3,607,244

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[21] Appl No. **710,767**
[22] Filed **Mar. 6, 1968**
[45] Patented **Sept. 21, 1971**
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[32] Priority **Mar. 11, 1967**
[33] **Japan**
[31] **42-15522**

[51] Int. Cl. **C22c 1/10,**
C22c 5/00
[50] Field of Search **75/173,**
135; 29/199; 200/166 C; 148/20.3

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[54] **ELECTRIC CONTACT MATERIAL AND METHOD**
OF MAKING THE SAME
6 Claims, No Drawings

[52] U.S. Cl. **75/173 R,**
148/20.3, 200/166

ABSTRACT: Electric contact material of the Ag-CdO type produced by forming Ag-CdO by an internal oxidation process including the addition of Fe or Sn or mixtures in specified amounts simultaneously with the melting of the Ag-Cd alloy.

ELECTRIC CONTACT MATERIAL AND METHOD OF MAKING THE SAME

BACKGROUND OF THE INVENTION

Compared with Ag which is widely in use, Ag-CdO contact material has an excellent antifusing property and an excellent wear-resisting property. Furthermore, it has the additional feature of the contact resistance being stabilized. Because of these merits, it is widely used as electric contact material for small and medium currents.

Generally, there are two methods for the manufacture of this electric contact material. One of the methods is a powder metallurgical method in which Ag powder and CdO powder are mixed, molded and sintered. The other is a method called the internal oxidation method in which Ag-Cd alloy is first produced by a general melting process and, after fabricating the alloy to the desired shape, the Cd which is the base metal in the alloy is selectively oxidized by heating in an oxidizing atmosphere.

Generally speaking, Ag-CdO contact material has been found to have the disadvantage of excessive arc wear when used for the contact of an electromagnetic switch for medium currents. When used for a contact in a medium-large current appliance to break current of several thousand amperes, it gets fused. Because of these disadvantages, the scope of its application has been limited.

It is the object of the present invention to eliminate the aforementioned disadvantage by adding the elements, Fe and Sn, to the Ag-CdO contact material manufactured by the internal oxidation heretofore employed.

It has been proven, as a result of experiments, that the contact material of this invention retains the advantage of low contact resistance of Ag-CdO contacts in general and yet enjoys the feature of far superior performance compared with Ag-CdO contact material with respect to arc wear and resistance to fusion in the regions of medium and large currents.

The results of tests on the contact properties of the material of this invention will be explained, with reference to the following examples.

EXAMPLE I

A Cd containing alloy comprising Ag—10 wt.-% CdO was made by melting, with an addition of 2 percent Fe at the time of melting.

The analytical values of this alloy were 8.75 percent Cd and 0.11 percent Fe. After casting it into a rod shape, the surface was removed and the rod was swaged at a high temperature (700–750° C) into a wire having a diameter of 6 mm. This was fabricated into a rivet having a neck diameter of 6 mm., a thickness of 3 mm., and a leg diameter of 3 mm.

Then the specimen was held for 30 hours in an electric furnace in which pure oxygen gas was caused to flow and which was kept at 800° C., whereby Cd and Fe in the alloy were selectively oxidized to obtain the final alloy.

Tests to compare the arc wear of this material with the material without the addition of Fe were carried out three times on each material under the following test conditions:

A.S.T.M. type contact property testing apparatus

Voltage AC 100 v, Current 30 a, Resistance load

Closing pressure 75 gr. Opening force 100 gr.

Results of measurement of the wear (mean values):

	Material without addition	Material with addition of Fe
Opening & Closing 100,000 times	3.0 mg.	2.4 mg.
200,000 times	7.0 mg.	5.3 mg.

In addition, a second Cd containing alloy of Ag—9 wt.-% CdO was made by melting in the same way and 1% Fe was added at the time of melting. The analytical values of this alloy

were 7.92% Cd and 0.03% Fe. After casting it into a rectangular shape, it was subjected to surface cutting and then press-bonded to an Ag base metal to obtain a specimen of 10×8×1.5 mm.

Then the final alloy was obtained by effecting internal oxidation in the same way as already described, and subjected to wear comparing tests under the following conditions:

Voltage AC 440 v., Current 300 a., power factor zero,

Rated 50 a. electromagnetic contractor

Results of measurement of arc wear:

	Material without addition	Material with addition of Fe
Opening & Closing 3000 times	88 mg.	60 mg.
Opening & Closing 5000 times	150 mg.	100 mg.
Opening & Closing 8000 times	8000	230 mg.
Opening & Closing 10000 times	280 mg.	10000 208 mg.

From the above, the improving effect of the addition of Fe with respect to wear is evidently recognized.

As is widely known, Fe has no solid solubility in both Ag and Cd. Consequently, Fe is present in the alloy only in a very small quantity with respect to the quantity charged. Moreover, it is considered to exist with the crystalline grains of Ag-Cd alloy in the form of a sort of mechanical mixture. It has been found that even such small quantities influence the constitution after oxidation, so that the crystalline grain size of Ag which is the base of the oxidized alloy becomes a fraction of that of the material without the addition of Fe and that the particles of separated-out CdO are distributed more spherically uniform.

It should be noted that the above tendency appears when the quantity of Fe is 0.01 percent or more. The quantity of Fe which can be melted in stably at the time of melting is 0.80 percent.

Therefore, it is necessary that the quantity of Fe in the alloy made by melting is 0.01 to 0.80 percent.

With regard to the quantity of CdO contained, it has been confirmed by other experiments that the effect of the addition of Fe is recognized irrespective of the content of CdO. Consequently, the material according to the present invention is not limited by the range of CdO content.

EXAMPLE II

Ag—10% Cd alloy with additions of 2% Sn and 1% Fe at the time of melting was prepared. The analytical values of Cd, Sn and Fe of this alloy were 10.3 percent, 1.95 percent and 0.02 percent, respectively. After casting it into a board shape, the surface cutting was made and an Ag base metal comprising 10 percent of the total thickness was press-bonded to only one side. The alloy was then rolled to 1.5 mm. and then punched to a diameter of 7 mm. The alloy was next held for 50 hours at 700° C. in an oxygen circulating atmosphere to selectively oxidize Cd, Sn and Fe in the alloy to obtain the final alloy.

The properties of this alloy are shown below in comparison with an alloy Ag—13% CdO formed by internal oxidation.

	Ag—13% CdO	Alloy of present invention	Pure silver
Specific gravity	10.1	10.1	10.5
Electric conductivity %TACS	72	70	107
Hardness (H v 5 kg.)	65	100	

It is a characteristic feature that the hardness is increased without lowering electric conductivity.

The material of the present invention which has the aforementioned alloy properties was compared with the material without the addition and was carried out with the contact testing apparatus of the A.S.T.M. type.

Testing Conditions

Voltage AC 100 v., Current 30 a., Resistance load
Closing force 75 gr., Opening force 100 gr.,
Opening and Closing frequency 60 times/min.

Test Results

The overall mean values for the amount of wear at six sets of contacts are as follows:

Material without the addition	Material of this invention	Unit mg.
7.1 mg.	3.8 mg.	

An analysis of the measurement distribution of the above results shows a significant difference. A remarkable effect to bring about improvement with respect to wear was recognized over material without the additions.

A specimen of 10×7×1.5 mm. was taken from the aforementioned board of 1.5 mm. thickness and subjected to the oxidation treatment in the same manner as described above to obtain a final alloy which was subjected to test under the following conditions:

Voltage AC 220 v., Current 220 a., Power factor 0.15, Installed in electromagnetic contactor of rating of 65 a., Opening & Closing frequency 1,600 times/hour, Charged 10 cycles

Test Results

Opening and Closing Times	Material without addition		Material of present invention	
	Fixed	Movable	Fixed	Movable
5,000	65.4 mg.	99.8 mg.	45.0 mg.	41.3 mg.
10,000	102.2 mg.	197.0 mg.	68.1 mg.	59.3 mg.
15,000	153.1 mg.	286.8 mg.	100.0 mg.	86.8 mg.
20,000	197.1 mg.	353.8 mg.	123.9 mg.	114.6 mg.
25,000	237.7 mg.	461.5 mg.	150.0 mg.	150.0 mg.
30,000	Fused together		180.8 mg.	184.0 mg.

From the above results it is shown that the material of this invention wears only about 40 percent as much as the material without the addition. In other words, it is shown that the material of this invention has a life more than two times longer.

Furthermore, the material without the addition got remarkably roughened on the surface and fused together 25,000 openings and closings times, so that it was no longer possible to continue the test on it. The material of this invention, however, had a smooth surface after 30,000 openings and closings and was in a condition fully capable of further testing.

The fusing property of the material of this invention was compared with the Ag—13% CdO internal oxidation alloy in the following manner.

A 5 mm. dia × 1.5 mm. piece of alloy made in the aforementioned way was brazed onto a Cu base; a damped wave of instantaneous 200 v., 1,400 a., was applied, time of charge 2 C/S, and contact pressure 200 gr. Under these conditions, the test was repeated 10 times.

In the above tests, fusing took place upon testing three times on the Ag—13% CdO internal oxidation alloy, while no fusing took place throughout the 10 tests on the material of this in-

vention. Its surface was in a condition still good for further tests.

It can be seen, therefore, that a great improvement with respect to wear was obtained in the opening and closing tests at a current of 30 a. or so, and at the same time a still more remarkable improvement with respect to wear and fusing was observed in the severe test of opening and closing a current of 200 a. or more.

As is widely known, Sn has a solid solubility in Ag and Cd. The composition of the examples of this embodiment is, therefore, a solid solution of Ag-Cd-Sn. On the other hand, Fe has no solid solubility in Ag and Cd. Its quantity entering the alloy is, therefore, very small, but it is considered to be present in the form of crystalline grains of the Ag-Cd-Sn alloy in the form of a sort of a mechanical mixture.

Even in a very small quantity, the presence of Fe influences the structure after oxidation and makes the crystalline grain size of Ag, the base of the oxidized alloy, finer.

On the other hand, the grains of dispersed oxides in the internal oxidation alloy of Ag-Cd-Sn, which has had only Sn added, are by far finer than those of the material without the addition. That is to say, Sn makes finer the dispersed oxides after the internal oxidation, while Fe makes the shape of the dispersed oxides spherical and at the same time makes finer crystalline grain size of the Ag base. The result is a hardness of a value of 100 or more of Vicker's hardness is obtained, a value greatly different from the 65 of the material without the addition.

The basic metal Ag has a tendency of melting and evaporating due to heat created by the arc which accompanies opening and closing, this being a principal cause for the roughening of and wear on the contact surface.

A material made of a metallic base in which particles of an oxide or the like which do not melt into the metal are dispersed is commonly called an alloy of the dispersion hardening type. It is effective to improve strength and resistance to heat. The smaller the sizes of both the dispersed grains and the crystalline grain are, the greater is the effect.

It is considered that the effect is similar in the case of the material of the present invention. That is to say, the addition of Sn and Fe makes the grains of the dispersed oxide and of basic Ag smaller, and it is considered that this improves both the heat resistance to arc and the strength of the basic metal Ag. It is observed, therefore, that the roughing of the contact surface is slight.

As regards the quantity of Sn added, an addition in the range of 0.5 percent–3 percent is adequate. It is not impossible to use it in a quantity of 3 percent or more. However, this will lower the melting point of the alloy and there will be a greater tendency that the alloy fuses at the temperature for internal oxidation.

It is not desirable to lower the treating temperature because the treatment will then take a very long time. Where Sn in a quantity exceeding 3 percent is added, it becomes impossible to effect internal oxidation and the phenomenon of external oxidation takes place. Sn addition in a quantity not exceeding 3 percent is, therefore, suitable for industrial purposes.

It has been confirmed that it is necessary the addition of Sn is in a quantity not less than 0.5 percent in order for the above-mentioned embodiments to have the desired properties mentioned in connection with the embodiments displayed clearly. It has also been confirmed that an increased ability to resist fusing, as outlined in the above embodiment, may be accomplished by the addition of Sn alone, without the addition of Fe.

As noted in example 1, the material of the present invention is not limited by the amount of CdO-content in the composition. Therefore, the desired effect upon the addition of Sn and Fe is observed irrespective of the quantity of CdO contained in the alloy.

In the embodiments of the present invention, it is permissible to have present, in small quantities, one or more of the following elements such as Ni, Co, Zn, In, Sb, Al, Mg, etc., without defeating the object of the present invention.

When the material of the present invention is as an electric contact material, it is often brazed to a basic metal such as Cu of the like. Consequently, it is one of the requirements of the electric contact material that it has a good brazing quality. The material of the present invention has, however, fine particles of oxide uniformly dispersed in the base of Ag, so that this dispersed oxide obstructs the wetting property of the brazing material and makes it impossible to effect a solid bonding with a basic metal. Therefore, in order to obtain a solid bond with the basic metal, a layer of pure Ag of a thickness of about 10 percent of the total thickness of the contact material is press-bonded to one surface of the material of this invention by hot-rolling. This press-bonding takes place before the internal oxidation to improve the brazing property of the material of this invention. Furthermore, the brazing property of the material of this invention may be further improved by the so-called one-side oxidation technique, in which an oxygen dispersion preventing material such as boric acid, boron, etc., produces a glasslike film at the temperature of internal oxidation. Alternately, a substance such as Al_2O_3 , MgO , etc., in fine particle form may be applied on one side of the material thereby producing an oxide film on one side of the material to permit brazing immediately before the internal oxidation. This allows internal oxidation to get underway from one side only and a thin unoxidized layer may be left only on the surface to be brazed. With the material having an Ag layer bonded on one side and the other side subjected to the oxidation process, it is impossible to distinguish, after the internal oxidation, which is the pure Ag layer side and which is the unoxidized alloy layer. This problem may be easily solved by marking the sides with stripes, dots or other identifiable indicia.

The melting point of the alloy of this invention before internal oxidation is approximately $800^\circ C.$, so that the temperature for internal oxidation is limited to $750^\circ C.$ or less. On the other hand, the internal oxidation is dependent on the dispersion of oxygen into the interior of the alloy, and the greater the speed of oxygen dispersion, the greater will be the thickness of the contact material that can be manufactured by the internal oxidation process. The dispersion speed is dependent on the temperature and the higher the temperature is, the greater the speed is. In the case of the material of this invention, however, the temperature for internal oxidation is lower than that for Ag-CdO materials in general, as already mentioned. Consequently, a 2-mm. thickness of contact material is the limit for industrial production if the ordinary internal oxidation technique, namely the treatment in air reflux, pure oxygen reflux, is employed. As mentioned in connection with the aforementioned examples, however, the material of this inven-

tion has excellent features for use with medium and large currents, so that a thickness in excess of 2 mm. may be required for the contact material. To overcome this problem, a material having a thickness of 4 mm. can be manufactured industrially by treating it in a reflux atmosphere of pure oxygen at 4 atmospheres pressure to increase the speed of oxygen dispersion into the alloy and obtain a thick material. That is to say, the manufacture on an industrial scale of the material of this invention having a large thickness has been made possible by effecting the internal oxidation in an oxygen atmosphere of a high pressure. It has also been discovered that the material of a still greater thickness can be manufactured by increasing the pressure of the oxygen atmosphere.

While the present invention has been described with reference to preferred embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the spirit and scope of the invention.

What is claimed is:

1. In a method for producing an electrical contact material of the Ag-CdO type by an internal oxidation process, including the step of forming an Ag-Cd alloy melt, the improvement which comprises melting an Ag-Cd alloy, adding to the alloy melt a member selected from the group consisting of Fe, Sn and mixtures thereof, casting said alloy to form the electrical contact shape and subjecting the alloy to internal selective oxidation to convert the Cd, Fe and Sn to their oxides, provided that the Fe is added to said alloy melt in an amount of from 0.01 to 0.03 wt.-% and that the Sn is added to said alloy melt in an amount of from 0.5 to 3.0 wt.-%
2. A method for producing an electrical contact material as in claim 1 wherein said material is producing in a high-pressure oxygen circulating atmosphere.
3. A method for producing an electrical contact material as in claim 1 wherein from 0.01 to 0.03 wt.-% Fe is added to said Ag-Cd melt, whereby an oxide of Fe is contained in the final material.
4. A method for producing an electrical contact material as in claim 3 wherein from 0.5 to 3.0 wt.-% Sn is additionally added to the Ag-Cd melt, whereby oxides of Fe and Sn are contained in the final material.
5. A method for producing an electrical contact material as in claim 1 wherein from 0.5 to 3.0 wt.-% Sn is added to the Ag-Cd melt whereby an oxide of Sn is contained in the final material.
6. The electrical contact material produced by the process of claim 1.